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IMPROVED ACTIVATION ANALYSIS OF TRACE ELEMENTS IN FRESH WATER SOLIDS*

by

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ELEMENTS IN FRESH WATER SOLIDS

ABSTRACT

Trace elements in water or solids can be easily determined
after neutron activation with the high-resolution lithium-drifted
germanium detector and gamma-gamma coincidence equipment. The
gamma energies are determined more precisely by the germanium
detector than is possible with sodium iodide detectors. Observed
activities are identified by comparing them with the known decay
characteristics of radioactive nuclides. The calculations do
not require computers, and the number of chemical separations
is reduced. This technique was used to determine, without
chemical separation, sodium, bromine, arsenic, chromium, iron,
cobalt, scandium, lanthanum, and zinc in particulate and evaporated
filtrate limnological samples.

INTRODUCTION

Trace elements can be accurately determined with neutron activation analysis. Methods for analyzing marine organisms have been reviewed by Fukai and Meinke (1959 and 1962). Methods for analyzing water for trace metals have been compared by Hume (1967). Neutron activation services, for a simple irradiation to the complete determination of complex samples, are now available commercially; 21 companies offering such services have been listed by Lyon and Miller (1967).

Most activation methods quantitatively determine the gammas emitted by the nuclides of interest. Interferences in complex gamma spectra can be minimized by electronically or mathematically subtracting known spectra from the sample spectrum -- denoted "spectrum stripping" -- and by chemically separating the mixture of nuclides. Both methods assume that the components of the mixture are known; neither is ideal for all mixtures. Activation techniques may become more applicable either by improving the chemical separation techniques or by improving the resolution of the gamma detection system. The high resolution of the lithium-drifted germanium detector improves the resolution.

This paper demonstrates the advantages of lithium-drifted germanium, Ge(Li), detectors, both alone and in conjunction with sodium iodide, NaI(Tl), detectors for gamma-gamma coincidence measurements. A description of the Ge(Li) detector system is given by Camp (1967). The high resolution (4 kev or better) of these detectors permits resolution of most of the gammas in activated samples; the energy and count rate of each photopeak can

be easily calculated. With gamma-gamma coincidence techniques, the observed gamma energies can be assigned to particular nuclides, and absolute counting is possible (Siegbahm 1965).

This paper presents techniques for determining trace elements in solid samples obtained from a fresh water pond. Sodium, bromine, arsenic, iron, cobalt, chromium, scandium, lanthanum, and zinc were determined simultaneously without chemical separation.

EXPERIMENTAL

Instruments and Detectors

Ge(Li) and NaI(Tl) gamma detectors were used. The Ge(Li) detector was manufactured by Isotopes, Inc. It is an 8 cm^2 by 10-mm-thick planar detector with a 3.7 kev resolution for the 1.3 Mev peak. The detector is cooled by liquid nitrogen; however, the first-stage field effect transistors in the preamplifier are at room temperature. The resolution could be increased by cooling the transistors, as reported by Cline (1967). The two detectors used for the gamma-gamma coincidence measurements were 3-inch-diameter by 3-inch-long NaI(Tl).

A 4096 channel analyzer, Nuclear Data, Inc., with a dual 4096 channel analog-to-digital converter (ADC) was used. A Tennelec TC-200 amplifier was used with the Ge(Li) detector. The dual ADC presented the coincidence data from both NaI(Tl) detectors to the analyzer; thus all coincidence data were available at one time.

Sample Preparation and Irradiation

The samples were solids filtered or evaporated from a fresh water pond. They were ashed to remove organic matter, weighed,

and wrapped in aluminum foil for irradiation. Pieces of the
aluminum foil were also irradiated as blanks because the solids
were not removed from the foil before counting. Some bromine
or arsenic activity may volatilize in ashing; however, this
possibility was not investigated.

The samples were placed in a water-tight aluminum capsule
and irradiated in a reactor to about 10^{17} neutrons/cm^2. Exposures
$>10^{17}$ neutrons/cm^2 would be required to increase the sensitivity
of the method so that elements with half-lives greater than 48
hours could be determined. Because of the high ^{24}Na activity
induced in the aluminum capsule, the samples decayed for six days
before they were counted.

Observed Gamma Spectra

The energies and assigned nuclides of the observed gamma
peaks are listed in Table 1. The nuclide assignments were based
on published decay schemes (Lederer, Hollander, and Perlman 1967),
half-lives, and known occurence in nature. The peaks in low
abundance were not assigned.

The gamma spectra of an evaporated filtrate, which had decayed
seven days, are shown in Figure 1. The two spectra illustrate the
advantage of the 3.7-kev resolution of Ge(Li) over the 60-kev
resolution of NaI(Tl) detectors. Even after seven days of decay
^{24}Na and ^{82}Br are still predominant. The ^{82}Br peak at 0.554 Mev
is about the same height as the ^{82}Br peak at 0.777 Mev. However,
the observed peak at 0.554 Mev was higher than that at 0.777 Mev
which indicated the presence of an additional nuclide. The
unresolved nuclide was deduced to be ^{76}As.

A gamma-gamma coincidence spectrum of the evaporated filtrate sample used in Figure 1 was made six and seven days after reactor discharge. The spectrum in Figure 2 was taken six days after reactor discharge and shows that the 1.37 Mev gamma is in coincidence with a 2.75 Mev gamma. The decay scheme, shown in Figure 3, indicates that ^{24}Na has these decay characteristics. The coincidence spectrum taken after seven days of decay, Figure 4 A and B, shows that the 0.777 Mev gamma is in coincidence with 0.554, 1.045, and 1.320 Mev gammas, and also the 0.554 Mev gamma is in coincidence with the 1.320 Mev gamma. The decay scheme in Figure 5 indicates that ^{82}Br has these decay characteristics. Other nuclides are identified by gamma energies, half-lives, and the known natural occurence of precursors in the activation reaction.

The gamma spectra of a particulate sample are shown in Figure 6. The coincidence spectrum after seven days of decay is similar to Figure 4 because ^{82}Br is still a major contributor. The coincidence of 0.487 and 1.596 Mev gammas confirmed the presence of ^{140}La. The coincidence spectrum after twenty days decay, Figure 7 A and B, shows that the 0.889 Mev gammas are in coincidence with the 1.120 Mev gammas, and the 1.173 Mev gammas are in coincidence with 1.332 Mev gammas. These coincidence gammas are assigned to ^{46}Sc and ^{60}Co, respectively.

<div align="center">CALCULATIONS AND RESULTS</div>

<div align="center">Calculations from Counting Data</div>

The disintegration rate of each nuclide was calculated from the Ge(Li) data. Each peak was taken to be 20 kev wide, and its baseline was taken to extend 10 kev on either side of the peak.

The count rates for the peak areas were corrected for the baseline count rate. The counting efficiencies for the various energies of gammas were determined by counting calibrated ^{110m}Ag and ^{60}Co sources. The branching ratios, half-lives, and abundances of the gammas for each nuclide were taken from Lederer, Hollander, and Perlman (1967). In the case of ^{76}As, the ^{82}Br contribution to the 0.554 Mev peak was calculated, and ^{76}As was reported as the difference. The ^{65}Zn concentration in Figure 6 was determined in a similar fashion.

Irradiation Calculations

The method of calculating the grams of naturally occurring nuclides in the sample is given in "Activation Analysis Handbook" by Koch (1960). The thermal cross sections were also taken from the Handbook. Since this irradiation was intended to determine the nuclides that were detectable, comparative standards were not run as they would be if the methods were put into routine use. The neutron exposure was determined by irradiating a known amount of cobalt along with the samples.

Results of Calculations

The results for ten samples, five particulate and five evaporated filtrate, are given in Table 2. (The samples are from different depths, and therefore not replicates.) The concentration is based on the weight of the solid sample after ignition and not on the amount of water filtered. The accuracy or precision of the method were not determined.

SUMMARY AND CONCLUSIONS

This study shows ways in which the usual neutron activation analysis methods can be improved. Chemical separations for many elements can be omitted if a high resolution Ge(Li) detector and an analyzer with a large number of channels are used. Nuclides can be assigned to observed gamma peaks easier by using a multi-parameter analyzer and two gamma detectors to determine which gammas are in coincidence. These improvements should reduce significantly the number of man-hours required per analysis.

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TABLE 1.   Observed Gamma Peaks and Assigned Nuclides

kev	nuclide	kev	nuclide
312		828	^{82}Br
320*	^{51}Cr	888*	^{46}Sc
330	^{140}La	1042	^{82}Br
336		1098*	^{59}Fe
347		1116*	$^{65}Zn + {}^{46}Sc$
412		1171	^{60}Co
487*	^{140}La	1290	^{59}Fe
496		1317	^{82}Br
554*	$^{82}Br + {}^{76}As$	1331*	^{60}Co
620	^{82}Br	1369*	^{24}Na
697	^{82}Br	1475	^{82}Br
776*	^{82}Br	1593	^{140}La
815	^{82}Br	1730	^{24}Na (escape peak)

* Peaks used in the calculations for the given nuclides.

TABLE 2. Concentration of Elements in Ashed Samples

	Co		Fe		Cr		La		Sc	
	c/m/mg	g/g sample (10^-6)	c/m/mg	g/g sample (10^-2)	c/m/mg	g/g sample (10^-4)	c/m/mg	g/g sample (10^-4)	c/m/mg	g/g sample (10^-4)
Particulate										
1	0.26	14	1.1	2.2	2.3	2.9	3.7	3.2	2.0	4.0
2	1.11	60	1.4	2.8	2.3	2.9	2.8	2.4	1.5	2.9
3	0.29	15	1.8	3.8	2.3	2.9	1.0	0.8	1.3	2.6
4	0.50	27	3.3	6.7	2.7	3.4	3.6	3.1	1.3	2.6
5	0.18	10	7.4	15.0	1.6	2.0	1.7	1.5	0.7	1.4
Evaporated Filtrate										
1	0.46	25	0.11	0.23	0.38	0.49	–	–	–	–
2	0.01	0.6	0.13	0.26	0.22	0.28	–	–	–	–
3	0.08	*	0.77	1.6	0.29	0.36	–	–	–	–
4	0.06	3	0.06	0.11	0.18	0.23	–	–	–	–
5	–	–	0.09	0.18	0.20	0.25	–	–	–	–

	Br		As		Na		Zn	
	c/m/mg	g/g sample (10⁻⁵)	c/m/mg	g/g sample (10⁻⁵)	c/m/mg	g/g sample (10⁻²)	c/m/mg	g/g sample (10⁻⁴)
Particulate								
1	1.7	3.8	0.50	0.68	6.6	0.67	0.24	4.0
2	2.1	4.7	0.23	0.31	8.8	0.89	0.22	3.7
3	0.6	1.4	3.8	5.1	12.0	1.2	0.20	3.3
4	3.2	7.4	1.0	1.4	10.6	1.1	0.08	1.3
5	2.4	5.5	2.7	3.6	3.0	0.3	0.38	6.3
Evaporated Filtrate								
1	22	52	12	16	56	5.7	0.06	1.0
2	23	53	10	13	56	5.7	0.01	0.2
3	12	28	5	7	25	2.5	0.05	0.8
4	21	47	9	12	49	4.9	0.03	0.5
5	18	40	19	26	42	4.3	—	—

Figure content labels:

Count Rate, Linear (y-axis)

Energy, Mev (x-axis)

0.554
82Br + 76As

0.619
82Br

0.777
82Br

0.700
82Br

0.828
82Br

1.045
82Br

1.320
82Br

1.478
82Br

1.369
24Na

1.731
escape peak
24Na

3" x 3"
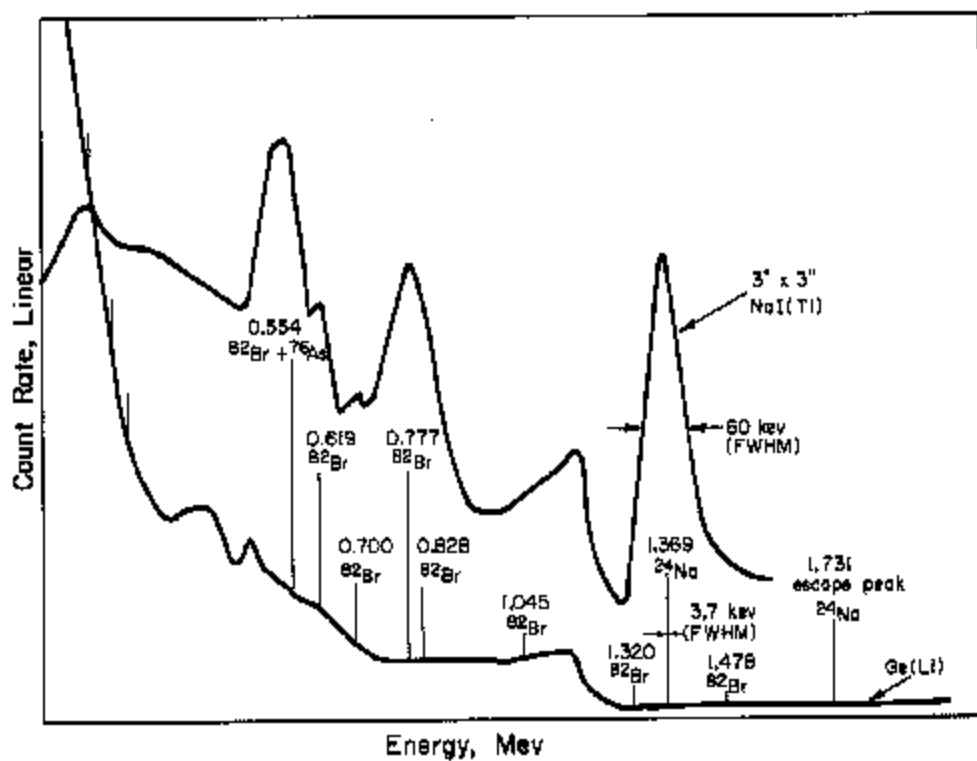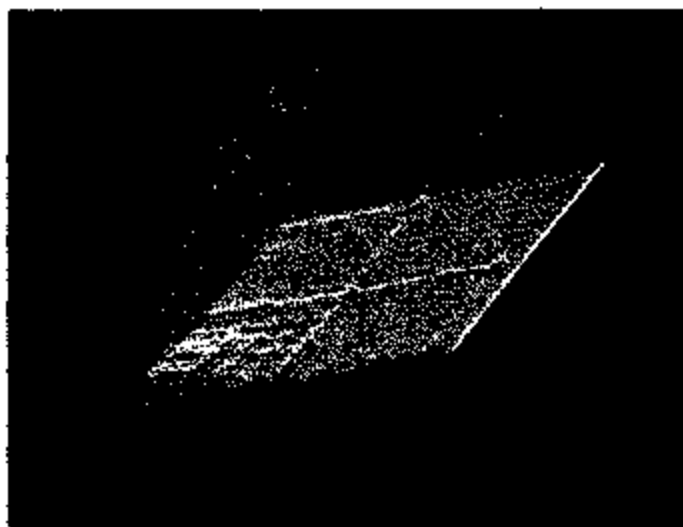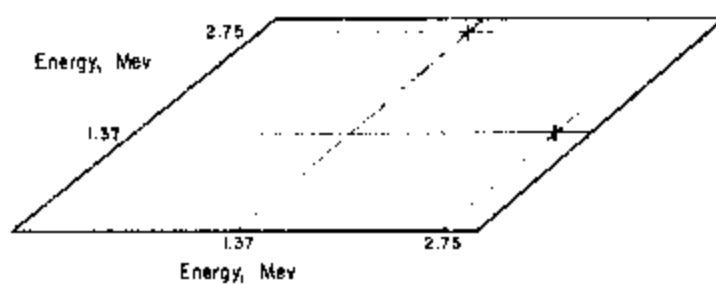NaI(Tl)

60 kev
(FWHM)

3.7 kev
(FWHM)

Ge(Li)

FIG. 1 GAMMA SCANS OF EVAPORATED FILTRATE SEVEN DAYS AFTER
DECAY COMPARING NaI(Tl) AND Ge(Li) DETECTORS

A

B

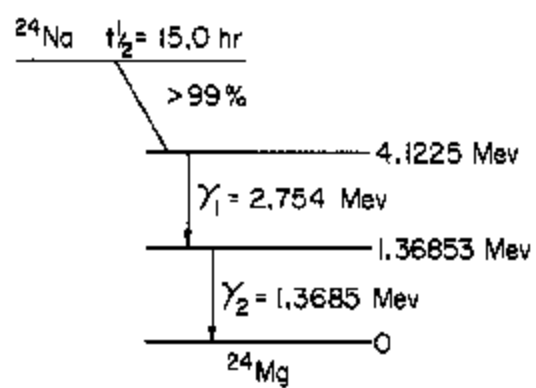FIG. 2 GAMMA-GAMMA COINCIDENCE SPECTRUM OF EVAPORATED
FILTRATE SIX DAYS AFTER DECAY

FIG. 3 DECAY SCHEME OF ^{24}Na

A

Energy, Me.

Energy, Me.

B

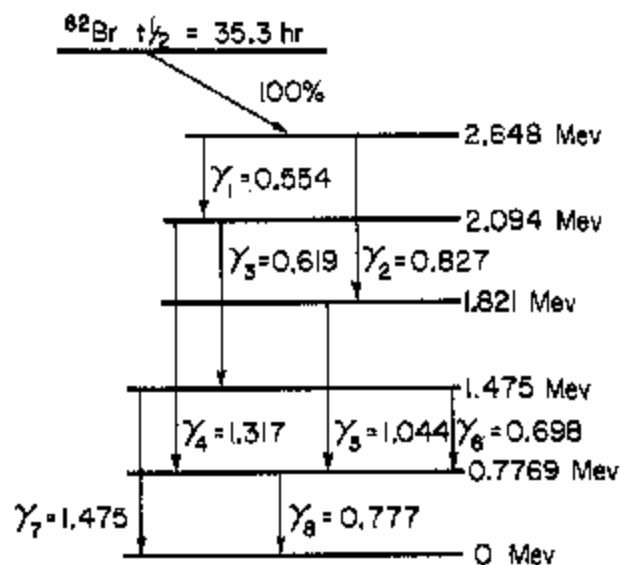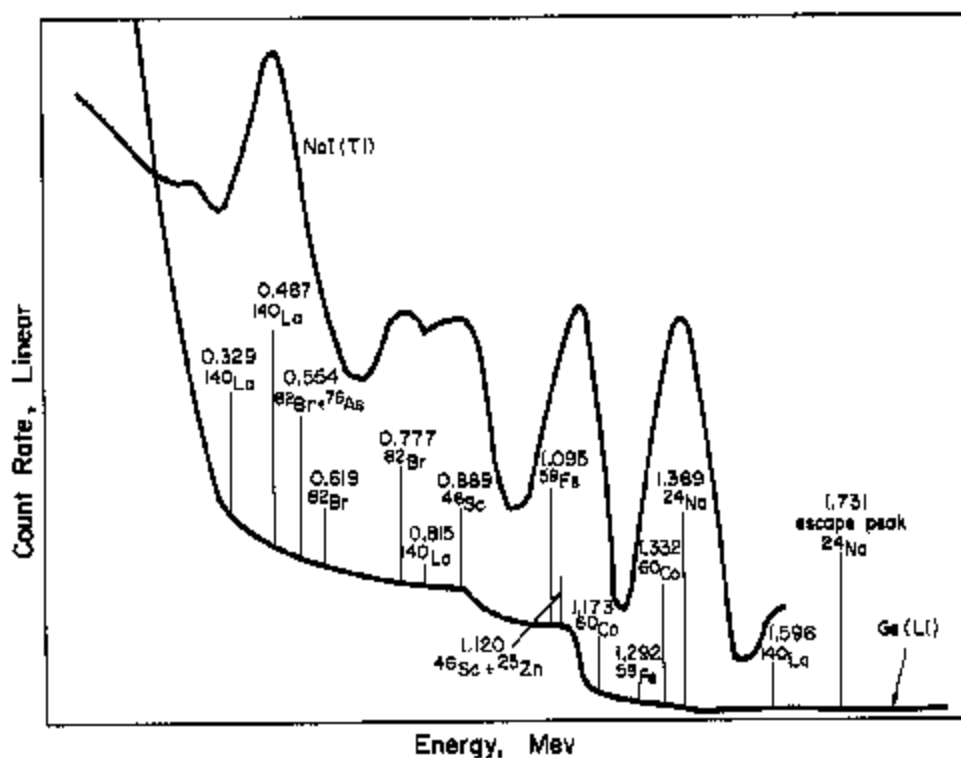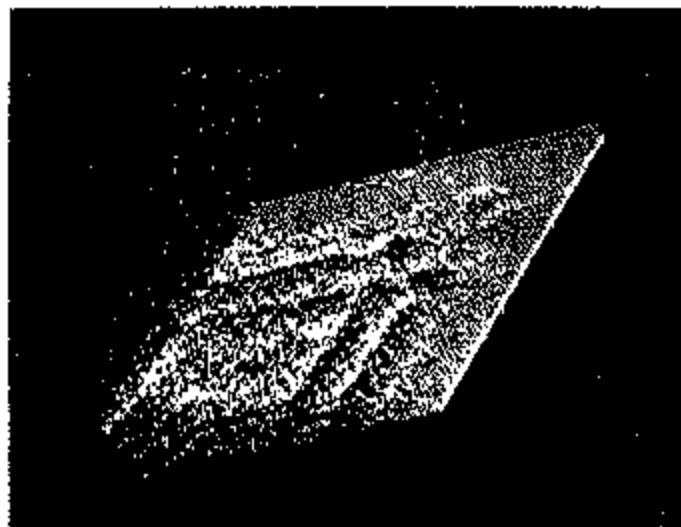FIG. 4 GAMMA-GAMMA COINCIDENCE SPECTRUM OF EVAPORATED
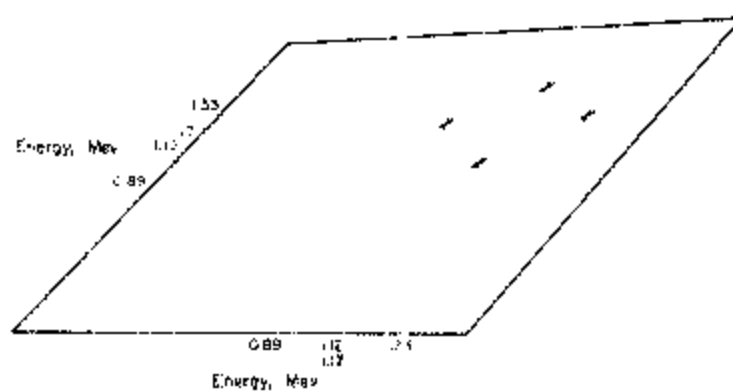FILTRATE SEVEN DAYS AFTER DECAY

FIG. 5 DECAY SCHEME OF ^{82}Br

FIG. 6 GAMMA SCAN OF PARTICULATE SAMPLE SEVEN DAYS AFTER
DECAY COMPARING NaI(Tl) AND Ge(Li) DETECTORS

A

Energy, Mev — 1.33, 1.12, 0.89

0.89, 1.12, 1.17, 2.1 — Energy, Mev

B

FIG. 7   GAMMA-GAMMA COINCIDENCE SPECTRUM OF PARTICULATE
SAMPLE TWENTY DAYS AFTER DECAY